Results of the 2005 NATA Model-to-Monitor Comparison, Final Report

Prepared by:

Eastern Research Group, Inc.
1600 Perimeter Park Drive
Morrisville, NC 27560

Prepared for:

Ms. Barbara Driscoll
U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
Research Triangle Park, NC 27711

December 17, 2010

DISCLAIMER

The information presented in this document is intended as a technical resource for EPA's National-Scale Air Toxics Assessment. The mention of commercial products, their source, or their use in connection with material reported herein is not to be construed as actual or implied endorsement of such products.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

1.0 INTRODUCTION

The purpose of this report is to summarize and present findings from the model-to-monitor study results for U.S. Environmental Protection Agency's (EPA) 2005 National-Scale Air Toxics Assessment. This report describes the methodology and procedure in comparing receptor-specific location concentrations of selected hazardous air pollutants (HAPs) with actual ambient monitoring data. The final results presented in this report are important in understanding the strengths and limitations of air toxics modeling, in particular to a national assessment.

1.1 Background

Acute and chronic exposure to specific hazardous air pollutants (HAPs) can lead to cancer and/or noncancer effects. Since the passage of the 1990 Clean Air Act Amendments (CAAA),[1] EPA has spent considerable time and resources establishing federal regulations, primarily through maximum achievable control technology (MACT) standards and Risk and Technology Review (RTR) activities, to reduce emissions for HAPs. Atmospheric models, such as those executed for the National-Scale Air Toxics Assessment (NATA), are often used to characterize the nation's air toxics problem both in absolute as well as relative senses by geographic area and pollutant.

One of the most robust methods for assessing what people may be breathing is through ambient air monitoring of HAPs. Ambient monitoring data can help identify pollutants and specific emission sources impacting an area's air quality and track changes or identify trends in ambient concentrations. Since 1990, the number of nationwide HAP monitors across the U.S. has increased dramatically (>50%). As a consequence, representativeness of people's inhalation exposure to HAPs has increased. However, the majority of HAP monitors are generally clustered in urban areas. For example, in 2005, ambient air monitoring for benzene, a national priority pollutant, occurred mainly in urban areas (Figure 1), accounting for less than 7% of all the counties in the country. This clustering of HAP monitors highlights the geographic disparity in truly assessing nationwide exposure.

[1] U.S. EPA. Clean Air Act Amendments. OAQPS. Internet address: http://www.epa.gov/air/oaq_caa.html/

EPA develops point source and county-level source emission inventories (area nonpoint, onroad mobile, nonroad mobile, and biogenic) for all geographic areas in the country. Due to the resources required for ambient monitoring of HAPs, it is not feasible to place monitors all over the country, let alone in each county. Thus, emissions modeling can be performed to generate model ambient concentrations. NATA modeling is the "bridge" to assess national-level exposure trends at all geographic locations across the country.

1.2 Report

This report demonstrates the approach for the model-to-monitor comparison and preliminarily evaluates the strengths/limitations of modeling specific HAPs. The following three questions were used to guide the study:

- Which pollutants are in good agreement between the ambient concentrations and the NATA model?
- Which pollutants are under-predicted between the ambient concentrations and the NATA model?
- Which pollutants are over-predicted between the ambient concentrations and the NATA model?

The report is organized into 4 sections. Table 1-1 presents the contents of each section.

Table 1-1. Organization of the 2005 NATA Model-to-Monitor Report

Report Section	Section Title	Overview of Contents
1	Introduction	This section serves as an introduction to the background and scope of the NATA model-to-monitor comparison.

Table 1-1. Organization of the 2005 NATA Model-to-Monitor Report (Cont.)

Report Section	Section Title	Overview of Contents
2	Data Sources and Methodology	This section provides information on the 2005 NATA model-to-monitor comparison: • Data sources • Annual averaging technique for ambient data
3	Results	This section presents and discusses the results of the 2005 NATA model-to-monitor comparison using various statistical metrics to assess the confidence in modeling results.
4	Conclusions	This section summarizes the most significant findings of the report, and presents the strengths and limitations of NATA model results.
A	HAPs Not Evaluated in this Assessment	This section lists the HAPs not included in this assessment due to limited or no measurements data for 2005.

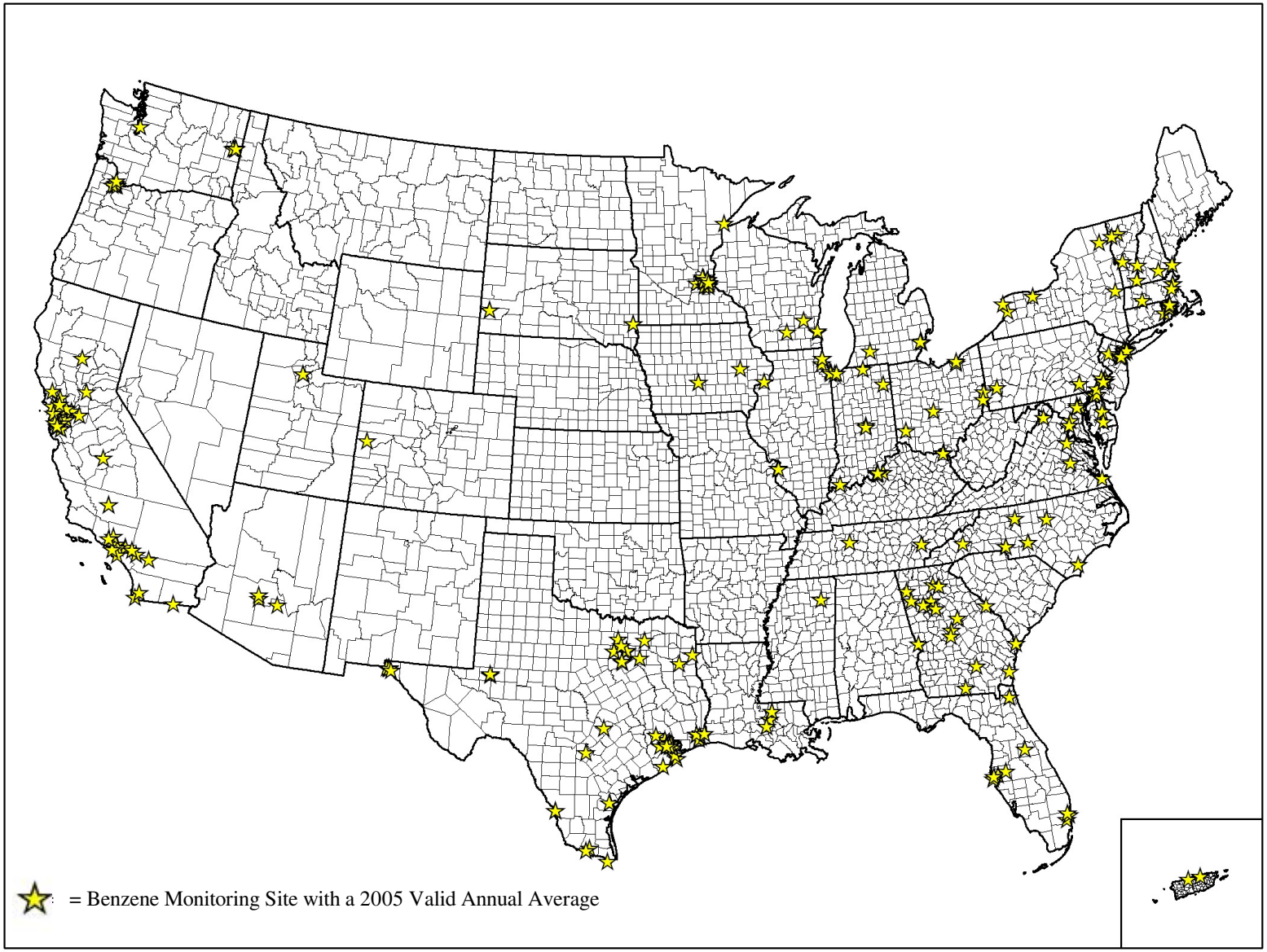

Figure 1-1. Benzene Monitors Across the U.S., 2005.

2.0 DATA SOURCES AND METHODOLOGY

NATA 2005 represents EPA's fourth national air toxics assessment. The first assessment began in 1996, and continued every three years (1999, 2002, and 2005) to match the triennial cycle of EPA's National Emissions Inventory (NEI) for HAPs. NATA is EPA's ongoing comprehensive evaluation of air toxics in the U.S. EPA developed the NATA as a state-of-the-science screening tool for State/Local/Tribal Agencies to prioritize pollutants, emission sources and locations of interest for further study in order to gain a better understanding of risks.[2]

NATA assessments do not incorporate refined information about emission sources, but rather, use general information about sources to develop estimates of risks which are more likely to overestimate impacts than underestimate them. NATA provides chronic estimates of the risk of cancer and other serious health effects from breathing (inhaling) air toxics in order to inform both national and more localized efforts to identify and prioritize air toxics, emission source types, and locations which are of greatest potential concern in terms of contributing to population risk. This in turn helps air pollution experts focus limited analytical resources on areas and/or populations where the potential for health risks are highest. Assessments include estimates of cancer and non-cancer health effects based on chronic exposure from outdoor sources, including assessments of non-cancer health effects for Diesel Particulate Matter (PM). Assessments provide a snapshot of the outdoor air quality in 2005 and the risks to human health that would result if air toxic emissions levels remained unchanged.

2.1 Data Sources

In this section, the important data sources used for this study are presented. Each data source is publicly available.

[2] U.S. EPA. National Air Toxics Assessment. OAQPS. Internet address: http://www.epa.gov/nata/

2.1.1 NEI Data

EPA compiles the NEI,[3] consisting of stationary (point and nonpoint area), mobile (onroad and nonroad), and biogenic source emissions for the entire United States, which are posted at the following website location: http://www.epa.gov/ttn/chief/eiinformation.html. These emission inventories are typically compiled and released every three years. In the past, due to the efforts required in obtaining, compiling, and reviewing by multiple stakeholder review, a base year inventory was finalized 3 to 5 years after the calendar end of the base year (e.g., the inventory data used for the 2005 NATA was finalized in 2010).[4] EPA has re-engineered the NEI for base year 2008 to help expedite this schedule.

Primary data sources for the NEI include:

- State, local, and tribal agency emission inventories;
- EPA's Maximum Achievable Control Technology (MACT) and Risk and Technology Review (RTR) Programs;
- Department of Energy's (DOE) Energy Information Agency (EIA) and EPA's Clean Air Markets Division (CAMD) Emission Tracking System/Continuous Emissions Monitoring (ETS/CEM) data for electric generating utilities (EGUs);
- EPA's Toxics Release Inventory (TRI);
- Data from other studies (e.g., trade associations, Bureau of Ocean Energy Management, Regulation, and Enforcement (BOEMRE) oil and natural gas platform data);
- Data calculated by EPA's Emission Inventory and Analysis Group (EIAG) staff (e.g., area nonpoint sources);
- Data calculated by EPA's MOVES and MOBILE models;
- Data calculated by EPA's Nonroad models, such as NONROAD, and Federal Aviation Administration (FAA) datasets;
- Data from EPA's biogenic emission models;
- Data carried forward from the previous inventory for gap-filling; and
- Data augmented through particulate matter (PM) and boiler HAP augmentation techniques.

Pollutants in the NEI consist of HAPs and criteria air pollutants (CAPs) and their precursors (CO, NH_3, NO_x, PM, SO_2, and VOCs). Base year inventories are typically compiled every three years; the first emission inventory used for NATA modeling was the 1996 NEI, with

[3] U.S. EPA. Emissions Inventories. OAQPS. Internet address: http://www.epa.gov/ttn/chief/eiinformation.html

[4] U.S. EPA. 2005 NATA National Emissions Inventory (NEI), Version 3. Data provided by A. Pope. OAQPS. September 2010.

subsequent inventories in 1999 and 2002. It is important to note that state, local, and tribal agency reporting thresholds are not consistent across the country. Certain source categories, such as dry cleaners or gas stations, may be reported at the individual point source level in one jurisdiction, but lumped together as an area nonpoint source at the county-level in another jurisdiction.

2.1.2 Ambient Air Monitoring Data

Air toxics ambient monitoring data for the year 2005 were initially extracted from EPA's Phase VI Air Toxics Archive.[5] This historical archive contains over 26 million HAP concentration records, spanning from 1973 to 2007. Additionally, 2005 year data from EPA's Air Quality Subsystem (AQS) were retrieved to identify new or updated data.

For the year 2005, which coincides with this assessment, there were over 2.9 million HAP ambient records at varying measurement levels (1-hour, 3-hour, 4-hour, and 24-hour measurements) at over 800 monitoring sites. Nearly 92% of the HAP records for 2005 sampling dates were originally retrieved from EPA's AQS and less than 7% were extracted from the Interagency Monitoring of Protected Visual Environments (IMPROVE). The remaining 2005 year data records (less than 2%) were taken from EPA's Phase V historical archive.[6]

2.1.3 2005 NATA Modeling

EPA made several methodological changes to the 2005 NATA assessment when compared to previous assessments. Although EPA is continually refining and updating the assessment methods, it is important to remember that NATA is a screening-level assessment. The intent is to identify HAPs resulting in high exposures or census tracts where population exposures may be of concern. These areas would then require more refined assessments, e.g., monitoring or site-specific risk assessments, to develop a more thorough understanding of these "hot-spot" exposures. NATA predicts ambient concentrations at over 66,000 census tracts across the U.S.

---

[5] U.S. EPA. Air Toxics Data. OAQPS. Internet address: http://www.epa.gov/ttn/amtic/toxdat.html#data

[6] U.S. EPA. Air Toxics Data Analysis 2003-2006 (partial). OAQPS. Internet address: http://www.epa.gov/ttn/amtic/toxdat.html#data

The following improvements have been made in the 2005 NATA:[7]

- Point Sources
  - The point source NATA inventory was based on 2005 emissions.
  - Risk and Technology Review emissions inventory updates were included.
  - Certain nonpoint categories are now modeled as point sources (i.e., forest and wildfires, chromium electroplating).
  - Data for 19,000 airports were included.
  - Landfill emissions updated/removed.
- Nonpoint sources
  - The 2005 NEI was generally unchanged from 2002 (few minor edits).
  - Emissions from forest fires and wildfires were removed.
  - Formaldehyde and benzene from pesticides were removed from the 2005 NEI inventory.
  - Chromium Electroplating sources were moved to the point source inventory.
  - Several minor adjustments to improve accuracy were made at the state/county level.
- Mobile Sources
  - The onroad and nonroad inventories were updated for 2005.
  - The new MOVES (Motor Vehicle Emission Simulator) emissions model was used for some HAPs.
- Modeling
  - The secondary formation of formaldehyde, acetaldehyde, and acrolein were predicted using the Community Multi-Scale Air Quality (CMAQ) model.
  - The transformation of 1,3 butadiene to acrolein was accounted for using CMAQ.
  - The mobile source modeling approach by using AERMOD was improved.
  - Emissions buoyancy for certain sources at coke oven facilities was accounted for.
- Risk Characterization
  - Dose-response values were updated with latest science (IRIS, CalEPA, ATSDR).
  - The formaldehyde unit risk estimate was revised.

In addition to the census-tract level ambient concentrations predicted by the NATA 2005, EPA used the model to develop specific receptor-level HAP concentrations for over 1,000 locations which coincided with locations of air toxics monitoring sites. These concentrations were the basis for the 2005 model-to-monitor comparison.

[7] Palma, T. E-mail Communication from Ted Palma, U.S. EPA to Regi Oommen, Eastern Research Group. September 7, 2010.

2.2 Methodology: Calculating An Annual Average

To properly compare ambient monitoring data to the modeled receptor concentrations, annual average concentrations which represent the year 2005 must be calculated. Because the emissions that were modeled were annual estimates, the model-to-monitor comparison must also reflect concentrations for an entire year by developing annual averages. Thus, from a temporal standpoint, it is not suitable to compare modeled concentrations (which are modeled from annual emissions) to ambient data that do not represent an entire year. Unfortunately, a sizeable amount of the 2005 ambient data records (47%) is: typically seasonal (e.g., measurements taken during the summer for ozone monitoring); not encompassing the entire year (e.g., sampling began mid-year); or is missing data (e.g., sample contamination or equipment failure). Nevertheless, annual averages can be calculated for 53% of the data (1.56 million records).

Annual averages are calculated using the following procedure:

1. Extract 2005 ambient HAP data from the Phase VI archive.
2. For sub-daily measurements, calculate valid daily concentrations.
3. Identify daily concentrations by site and pollutant which represent an entire year.
4. Calculate annual average by HAP by site from the daily averages (including zeroes for non-detects).

Calculating Daily Averages

Initially, over 2.9 million concentration records were extracted for the 2005 year from the Phase VI archive and the AQS supplement. Because these records were at differing temporal measurements, all records were converted to daily records, and the units were standardized to micrograms per cubic meter ($\mu g/m^3$). Sub-daily measurements (which accounted for over 55% of the 2005 records) must have at least 75% temporal coverage within a day. To be considered a valid daily average, the following criteria need to be met:

1. At least eighteen of twenty-four 1-hour measurements must have a detected concentration.
2. At least six of eight 3-hour measurements must have a detected concentration.
3. At least five of six 4-hour measurements must have a detected concentration.

Based on these criteria, over 687,000 valid daily records were compiled.

Calculating Annual Averages

Valid daily averages were then reviewed by site and HAP to assess whether there was adequate temporal coverage. To assess temporal coverage, we used a two-step procedure:

1. Ensured that within each calendar quarter (January 1-March 31, April 1-June 30, July 1-September 30, and October 1-December 31), six of eight prescribed sub-quarter zones by site and HAP must have a valid daily concentration.
    a. This approach allowed sites which sampled once every twelve days (which, in theory, yields a minimum of seven sampling days in a calendar quarter) to be included.
    b. Sites which sampled more frequently than once every twelve days, such as 1-in-6 days or 1-in-3 days, would also meet this "sub-quarter zone" temporal coverage.
2. Ensured that a valid annual average by site and HAP consisted of three valid calendar quarters.

Once the valid daily averages met both of the above criteria, an annual average, which is simply the average of detected concentrations and non-detects, was calculated. For non-detects, a zero value was used as a surrogate prior to calculating valid annual averages. This is another deviation from the 2002 NATA model-to-monitor comparison which used one-half the pollutant method detection limit as a surrogate for non-detects in calculating the annual average.[8] In total, 5,621 annual averages were calculated for 2005.

2.3 Methodology: Ambient Pollutant Considerations

After all the annual averages were calculated by HAP, certain pollutants were grouped or designated in order to properly compare with the NATA modeled concentrations. The following groupings and designations were performed:

- Xylenes: Annual averages of the xylene species (*m*-, *o*-, and *p*-) were summed together to calculate a "Xylenes, total" pollutant group. This is appropriate because the individual risk for each specie is the same.

[8] U.S. EPA. Comparison of the 2002 Model-Predicted Concentrations to Monitored Data. OAQPS. Internet address: http://www.epa.gov/ttn/atw/nata2002/02pdfs/2002compare.pdf

- Polycyclic Organic Matter (POM): Annual averages of POM species were summed together by their risk ranges into prescribed POM Groups.[9] The following POM groups were used:

    - POM Group 2: Consists of 9H-fluorene; acenaphthene; acenaphthylene; anthracene; benzo(e)pyrene; benzo(g,h,i)perylene; fluoranthene; perylene; phenanthrene; and pyrene.
    - POM Group 5: Consists of benzo(a)pyrene and dibenzo(a,h)anthracene.
    - POM Group 6: Consists of benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, and indeno(1,2,3-cd)pyrene.
    - POM Group 7: Consists of chrysene.

- Metal HAPs: NATA results do not distinguish between PM_{10}, $PM_{2.5}$, or total suspended particles (TSP) species for the modeled metals concentrations. For this assessment, annual average concentrations for PM_{10} metals were chosen, as health-based comparison levels were available for this range, which is considered to be in the respirable range. Because there are national ambient air quality standards (NAAQS) for lead, the NATA lead results were compared to both lead (PM_{10}) and lead (TSP) ambient annual averages in this study. In the 2002 assessment, model-to-monitor ratios for the metals were presented for the $PM_{2.5}$ and TSP size fractions. This data was primarily from monitors in the IMPROVE network, which are typically situated in Federal Class 1 and Class 2 areas (e.g., national parks, protected areas); these areas are rural and pristine and typically have few anthropogenic emission sources.

- PM_{10} Metals: PM_{10} metals data were reported in either "local conditions" (not adjusted for temperature and pressure) or "standard conditions" (adjusted to standard temperature and pressure conditions). Annual average concentrations for PM_{10} metals that were in "local conditions" were not adjusted for standard temperature and pressure and were considered the same in this comparison.

- Chromium: NATA presents chromium results as either trivalent or hexavalent species. Hexavalent is the chromium specie of concern due to its health risk. For this assessment, chromium (PM_{10}) consists of the NATA trivalent chromium specie plus the NATA hexavalent chromium specie. Where hexavalent chromium data was available from the ambient data, it is compared to the NATA hexavalent chromium specie modeled concentration.

- Acrolein: EPA will not use the acrolein data in evaluating the potential for health concerns from exposure to air toxics in outdoor air as part of this study. The Agency made this determination after results of a short-term laboratory study raised questions

[9] U.S. EPA. Health Effects Information Used In Cancer and Noncancer Risk Characterization For the 1999 National-Scale Assessment. Internet address: http://www.epa.gov/ttn/atw/nata1999/99pdfs/healtheffectsinfo.pdf

about the consistency and reliability of monitoring results of acrolein. More information is available at http://www.epa.gov/schoolair/acrolein.html.

2.4 Methodology: NATA Pollutant Considerations

In reviewing the receptor-location HAP concentrations from the NATA model, two adjustments were made:

- Xylenes: NATA presents results for xylenes for the following designations: xylenes (mixed), *m*-xylene, *o*-xylene, and *p*-xylene. A careful review of these data indicates that there was no double-counting between the "mixed" concentration and the individual isomers of "*m*-, *o*-, and *p*-". The reason for the four designations is that some of the underlying emission inventory data did not distinguish between the isomers, and thus NATA made no assumption about its breakdown. Thus, all of the NATA results for xylenes were summed together at each receptor location and compared to the summed xylene concentrations at that same receptor.

- Metals: Similar to xylenes, NATA presents metal results primarily as "compounds". For example, NATA results for manganese may be: manganese compounds; manganese dioxide; manganese nitrate; manganese sulfate; manganese tetroxide; and manganese trioxide. A careful review of these data indicates that there was no double-counting between the "compounds" and the individual manganese pollutants. Similar to above, the reason for the multiple designations is that some of the underlying emission inventory data reported more specific manganese compounds than the general total compounds. Thus, all of the NATA results for the individual metals were summed together by metal compound at each receptor location and compared to the metal PM_{10} concentrations at that same receptor.

3.0 2005 MODEL-TO-MONITOR RESULTS

A model-to-monitor ratio is simply the modeled concentration divided by the annual average concentration. A model-to-monitor ratio close to 1 for a particular HAP at a monitoring site indicates a high level of confidence in the modeling results for that HAP and monitoring site. Similarly, an average model-to-monitor ratio of several monitoring sites closer to 1 can indicate a high level of confidence in the modeling results. Another metric which can be useful in understanding the results is the median (50^{th} percentile) model-to-monitor ratio. A median model-to-monitor ratio closer to 1 implies the model overestimates the ambient concentrations about as often as it underestimates them. A third metric to evaluate the model-to-monitor ratios is the closeness of the distribution statistics, such as the interquartile range (the range between the 25^{th} and 75^{th} percentile values). A tighter inter-quartile range can indicate more confidence in the model results. Finally, the "percent of sites underestimated" is the percent of sites for which the model-to-monitor ratio is below 1.

Table 3-1 presents the average model-to-monitor ratios for 68 pollutants, as well as the number of monitors and selected distribution percentiles from the 5^{th} to the 95^{th} percentiles. HAPs which either did not have any detections nor enough detections to calculate an annual average in 2005 are presented in Appendix A.

Toluene, benzene, methyl chloride, 1,3-butadiene, formaldehyde, bromomethane, and 2,2,4-trimethylpentane had average model-to-monitor ratios between 0.9 to 1.1. Expanding the range from 0.8 to 1.2 adds xylenes, carbon tetrachloride, methyl-*tert*-butyl ether, *cis*-1,3-dichloropropylene, *trans*-1,3-dichloropropylene, and naphthalene. Table 3-1 also presents median model-to-monitor ratios. Carbon tetrachloride and methyl chloride median model-to-monitor ratios were between 0.9 to 1.1, while expanding that range from 0.8 to 1.2 adds toluene, benzene, acetaldehyde, and bromomethane. Gaseous HAPs tended to have average and median ratios closer to 1 than the metal HAPs. Metal PM_{10} average model-to-monitor ratios ranged from 0.120 (antimony PM_{10}) to 15.305 (beryllium PM_{10}). The chromium PM_{10} average model-to-monitor ratio is the closest (0.721) of all metals to 1.

Table 3-1. 2005 Model-to-Monitor Comparison Statistics

Type	Pollutant	# Monitors	5th Percentile	10th Percentile	25th Percentile	50th Percentile	75th Percentile	90th Percentile	95th Percentile	Average
Gaseous	Toluene	297	0.270	0.398	0.576	0.804	1.241	1.795	2.360	1.065
Gaseous	Benzene	296	0.364	0.446	0.628	0.825	1.146	1.583	2.152	0.982
Gaseous	Xylenes	266	0.104	0.207	0.364	0.632	0.966	1.599	2.255	1.159
Gaseous	Ethylbenzene	244	0.065	0.147	0.287	0.466	0.765	1.300	1.968	1.265
Gaseous	Carbon tetrachloride	222	0.839	0.906	0.939	1.016	1.173	1.304	1.588	1.131
Gaseous	Methyl chloride	206	0.764	0.842	0.914	1.030	1.181	1.316	1.509	1.083
Gaseous	Styrene	195	0.021	0.058	0.178	0.397	0.762	1.752	3.329	1.403
Gaseous	Methylene chloride	190	0.176	0.262	0.395	0.524	0.693	1.422	2.046	0.726
Gaseous	1,3-Butadiene	176	0.168	0.267	0.425	0.697	0.955	1.817	2.602	0.962
Gaseous	Tetrachloroethylene	174	0.126	0.165	0.289	0.449	0.687	0.933	1.308	0.560
Gaseous	Chloroform	169	0.211	0.243	0.383	0.554	0.807	1.792	2.124	0.746
Gaseous	1,1,1-Trichloroethane	163	0.451	0.624	1.166	1.622	3.993	5.399	5.659	2.646
Gaseous	*n*-Hexane	162	0.040	0.091	0.160	0.262	0.439	0.789	1.100	0.398
Gaseous	Formaldehyde	162	0.352	0.416	0.610	0.783	1.001	1.634	2.302	0.923
Gaseous	Acetaldehyde	160	0.506	0.631	0.878	1.159	1.439	1.787	2.294	1.235
Gaseous	Trichloroethylene	145	0.066	0.081	0.185	0.411	0.901	1.243	1.483	0.562
Gaseous	Bromomethane	143	0.112	0.141	0.316	0.817	1.244	1.553	1.675	0.979
Gaseous	2,2,4-Trimethylpentane	111	0.102	0.145	0.215	0.491	1.115	2.371	2.845	0.941
Gaseous	Ethylene dichloride	111	0.010	0.015	0.066	0.092	0.222	0.665	0.769	0.237
Gaseous	*p*-Dichlorobenzene	102	0.051	0.055	0.113	0.226	0.546	0.961	1.346	0.435
Gaseous	Chlorobenzene	102	<0.001	<0.001	0.003	0.005	0.021	0.037	0.089	0.017
Gaseous	Propionaldehyde	98	0.007	0.012	0.029	0.060	0.130	0.185	0.328	0.095
Gaseous	Methyl *tert*-butyl ether	88	0.012	0.026	0.088	0.567	0.930	1.850	2.517	0.800
Gaseous	Vinyl chloride	87	<0.001	0.002	0.009	0.026	0.089	0.405	0.715	0.143
Gaseous	Cumene	78	0.001	0.002	0.003	0.009	0.195	0.578	1.176	0.211
Gaseous	*Cis*-1,3-Dichloropropylene	77	<0.001	0.003	0.003	0.149	1.066	2.992	3.929	0.850
Gaseous	*Trans*-1,3-Dichloropropylene	77	<0.001	0.002	0.004	0.156	1.066	2.992	3.929	0.849
Gaseous	1,1,2,2-Tetrachloroethane	74	0.007	0.008	0.027	0.080	0.089	0.096	0.125	0.067
Gaseous	Ethylene dibromide	73	<0.001	0.001	0.005	0.017	0.028	0.036	0.050	0.029

Table 3-1. 2005 Model-to-Monitor Comparison Statistics (Continued)

Type	Pollutant	# Monitors	5th Percentile	10th Percentile	25th Percentile	50th Percentile	75th Percentile	90th Percentile	95th Percentile	Average
Gaseous	1,1,2-Trichloroethane	69	<0.001	<0.001	<0.001	0.003	0.004	0.011	0.018	0.011
Gaseous	Propylene dichloride	67	0.003	0.003	0.013	0.025	0.038	0.044	0.065	0.031
Gaseous	Vinylidene chloride	65	<0.001	<0.001	<0.001	0.004	0.004	0.007	0.010	0.011
Gaseous	Ethylidene dichloride	65	<0.001	<0.001	0.004	0.005	0.006	0.020	0.029	0.008
Gaseous	Methyl isobutyl ketone	63	0.007	0.009	0.019	0.105	0.486	2.468	3.782	5.386
Gaseous	Carbon disulfide	53	<0.001	<0.001	<0.001	0.002	0.007	0.020	0.049	0.010
Gaseous	Acrylonitrile	49	0.005	0.006	0.008	0.015	0.037	0.052	0.066	0.023
Gaseous	Chloroprene	46	<0.001	<0.001	<0.001	0.004	0.005	0.005	0.006	0.003
Gaseous	1,2,4-Trichlorobenzene	22	<0.001	<0.001	<0.001	<0.001	0.013	0.021	0.114	0.019
Gaseous	Hexachlorobutadiene	21	<0.001	<0.001	<0.001	<0.001	<0.001	0.004	0.011	0.003
Gaseous	Vinyl Acetate	20	<0.001	<0.001	<0.001	<0.001	0.001	0.002	0.008	0.005
Gaseous	Ethyl chloride	18	<0.001	<0.001	<0.001	0.003	0.009	0.034	0.073	0.013
Gaseous	Acetonitrile	17	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Gaseous	Ethylene oxide	14	0.005	0.006	0.008	0.013	0.016	0.017	0.018	0.012
Gaseous	Naphthalene	14	0.074	0.090	0.123	0.312	0.667	1.353	4.918	1.173
Gaseous	POM (Group 2)	14	0.007	0.011	0.016	0.023	0.048	0.111	0.135	0.045
Gaseous	Benzyl chloride	8	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Gaseous	POM (Group 7)	7	0.078	0.089	0.227	0.387	0.443	0.492	0.493	0.327
Gaseous	POM (Group 6)	7	0.071	0.079	0.160	0.264	0.289	0.953	1.449	0.453
Gaseous	Tribromomethane	7	<0.001	<0.001	<0.001	<0.001	<0.001	0.004	0.008	0.002
Gaseous	POM (Group 5)	6	0.347	0.549	1.014	1.368	1.606	3.439	4.345	1.785
Gaseous	Bis(2-Ethylhexyl)Phthalate	4	0.074	0.076	0.082	0.085	0.088	0.091	0.092	0.084
Gaseous	Chlorine	4	<0.001	<0.001	<0.001	<0.001	0.036	0.099	0.120	0.036
Gaseous	Biphenyl	4	0.013	0.019	0.038	0.060	0.148	0.285	0.331	0.126
Gaseous	Dibenzofuran	3	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Gaseous	Phenol	1	0.507	0.507	0.507	0.507	0.507	0.507	0.507	0.507
TSP-Metals	Lead (TSP)	123	0.019	0.032	0.079	0.161	0.298	0.521	0.821	0.240
TSP-Metals	Chromium VI	18	3.837	4.240	7.018	11.273	15.026	21.402	30.878	12.488

Table 3-1. 2005 Model-to-Monitor Comparison Statistics (Continued)

Type	Pollutant	# Monitors	5th Percentile	10th Percentile	25th Percentile	50th Percentile	75th Percentile	90th Percentile	95th Percentile	Average
PM_{10}-Metals	Manganese (PM_{10})	38	0.048	0.073	0.138	0.230	0.350	0.704	0.981	0.401
PM_{10}-Metals	Nickel (PM_{10})	37	0.080	0.096	0.153	0.379	0.621	1.044	1.299	0.496
PM_{10}-Metals	Lead (PM_{10})	37	0.113	0.122	0.227	0.311	0.435	0.599	0.822	0.356
PM_{10}-Metals	Arsenic (PM_{10})	37	0.208	0.234	0.441	0.518	0.684	0.848	0.993	0.563
PM_{10}-Metals	Chromium (PM_{10})	36	0.066	0.124	0.218	0.356	0.696	1.899	2.654	0.721
PM_{10}-Metals	Cadmium (PM_{10})	32	0.225	0.316	0.405	0.611	0.929	1.114	1.157	0.671
PM_{10}-Metals	Beryllium (PM_{10})	26	0.878	2.411	4.580	9.859	25.124	34.090	39.169	15.305
PM_{10}-Metals	Selenium (PM_{10})	26	0.055	0.069	0.098	0.191	0.299	0.422	0.869	0.259
PM_{10}-Metals	Cobalt (PM_{10})	25	0.063	0.108	0.173	0.245	0.806	1.370	1.730	0.558
PM_{10}-Metals	Antimony (PM_{10})	17	0.007	0.007	0.013	0.083	0.117	0.310	0.509	0.120
PM_{10}-Metals	Mercury (PM_{10})	2	0.181	0.190	0.216	0.259	0.302	0.328	0.337	0.259

Table 3-2 presents additional summary statistics of the model-to-monitor ratios, such as a percentage of monitors whose modeled concentrations are within 10%, 20%, and 30% of the annual average concentration. For example, the "percent of sites estimated within 30%" is the percent of sites for which the model-to-monitor median ratio is between 0.7 and 1.3. More than half of the carbon tetrachloride monitoring sites were within 10%, 20%, and 30% (52% of the monitoring sites within 10%, 75% within 20%, and 87% within 30%, respectively). Similarly, more than half of the methyl chloride monitoring sites were within 20% and 30% (70% within 20% and 85% within 30%, respectively). These trends show the consistency of the model results for these pollutants. No other pollutants have the majority of their monitoring results within these percentages. Less than one-tenth of all model-to-monitor ratios were: within 10%; less than one-fifth were within 20%; and nearly one-fourth were within 30%.

The percent of sites estimated "within a factor of 2" is the percent of sites for which the model estimate is somewhere between half and double the monitor average. HAPs in which 80% of their monitors were within a factor of 2 were benzene (82%), carbon tetrachloride (95%), methyl chloride (98%), and acetaldehyde (87%). "Factor of 2" ratios (ratios between 0.5 and 2.0) accounted for 44% of the model-to-monitor ratios. Figures 3-1 through 3-3 present the distribution statistics (25^{th}, 50^{th}, 75^{th}, and average model-to-monitor ratios) for each HAP. Figure 3-1 presents gaseous HAPs with greater than 100 monitors. Figure 3-2 presents gaseous HAPs with between 25 and 100 monitors. Finally, Figure 3-3 presents metal HAPs with a minimum of 25 monitors.

In each figure, the pollutants are organized by the highest to lowest number of monitors per pollutant; this side-by-side display of pollutants facilitates comparison to indicate which pollutants are being overestimated and underestimated, and which are estimated consistently. To interpret these whisker-type plots, the bottom of the statistic is the 25^{th} percentile, the top of the statistic is the 75^{th} percentile, the horizontal line in the middle is the median (i.e., 50^{th} percentile), and the "x" is the average model-to-monitor ratio. The yellow area represents the "factor of two" range. If the model consistently agrees with the monitored data for the pollutant, the 25^{th} and 50^{th} percentile lines will be narrow and centered at 1. As in the 1996, 1999, and 2002 comparisons,

Table 3-2. 2005 Model-to-Monitor Analysis Statistics

Type	Pollutant	# Monitors	Average % Difference	% Monitors Within 10%	% Monitors Within 20%	% Monitors Within 30%	% Monitors Within Factor of 2	% Monitors Under-estimated
Gaseous	Toluene	297	6.5	10.8	24.6	39.1	75.1	66.7
Gaseous	Benzene	296	-1.8	15.2	32.1	48.3	81.8	65.5
Gaseous	Xylenes	266	15.9	8.3	19.5	27.8	59.0	76.7
Gaseous	Ethylbenzene	244	26.5	6.1	12.7	19.7	41.0	85.2
Gaseous	Carbon tetrachloride	222	13.1	52.3	75.2	86.9	95.0	48.2
Gaseous	Methyl chloride	206	8.3	35.4	70.4	85.0	97.6	43.2
Gaseous	Styrene	195	40.3	6.2	10.8	15.4	32.3	83.1
Gaseous	Methylene chloride	190	-27.4	2.1	4.2	11.1	47.9	85.3
Gaseous	1,3-Butadiene	176	-3.8	8.0	17.0	31.3	56.3	76.1
Gaseous	Tetrachloroethylene	174	-44.0	5.7	12.6	19.5	42.0	92.0
Gaseous	Chloroform	169	-25.4	4.1	11.8	18.3	55.0	81.1
Gaseous	1,1,1-Trichloroethane	163	164.6	4.3	11.0	12.9	62.6	18.4
Gaseous	*n*-Hexane	162	-60.2	1.9	6.2	6.2	17.9	93.2
Gaseous	Formaldehyde	162	-7.7	10.5	30.9	47.5	76.5	74.7
Gaseous	Acetaldehyde	160	23.5	16.9	35.0	49.4	86.9	36.3
Gaseous	Trichloroethylene	145	-43.8	11.0	15.9	22.1	40.7	79.3
Gaseous	Bromomethane	143	-2.1	14.0	23.8	37.1	65.7	62.2
Gaseous	2,2,4-Trimethylpentane	111	-5.9	5.4	11.7	17.1	35.1	73.9
Gaseous	Ethylene dichloride	111	-76.3	0.0	3.6	6.3	15.3	98.2
Gaseous	*p*-Dichlorobenzene	102	-56.5	2.0	6.9	8.8	25.5	91.2
Gaseous	Chlorobenzene	102	-98.3	0.0	0.0	0.0	0.0	100.0
Gaseous	Propionaldehyde	98	-90.5	0.0	0.0	0.0	2.0	100.0
Gaseous	Methyl *tert*-butyl ether	88	-20.0	9.1	17.0	25.0	43.2	78.4
Gaseous	Vinyl chloride	87	-85.7	0.0	2.3	3.4	6.9	97.7
Gaseous	Cumene	78	-78.9	0.0	1.3	2.6	10.3	93.6
Gaseous	*Cis*-1,3-Dichloropropylene	77	-15.0	1.3	1.3	3.9	16.9	74.0
Gaseous	*Trans*-1,3-Dichloropropylene	77	-15.1	1.3	1.3	3.9	16.9	74.0
Gaseous	1,1,2,2-Tetrachloroethane	74	-93.3	0.0	0.0	0.0	0.0	100.0
Gaseous	Ethylene dibromide	73	-97.1	0.0	0.0	0.0	1.4	100.0

Table 3-2. 2005 Model-to-Monitor Analysis Statistics (Continued)

Type	Pollutant	# Monitors	Average % Difference	%Monitors Within 10%	%Monitors Within 20%	%Monitors Within 30%	%Monitors Within Factor of 2	%Monitors Under-estimated
Gaseous	1,1,2-Trichloroethane	69	-98.9	0.0	0.0	0.0	1.4	100.0
Gaseous	Propylene dichloride	67	-96.9	0.0	0.0	0.0	0.0	100.0
Gaseous	Vinylidene chloride	65	-98.9	0.0	0.0	0.0	0.0	100.0
Gaseous	Ethylidene dichloride	65	-99.2	0.0	0.0	0.0	0.0	100.0
Gaseous	Methyl isobutyl ketone	63	438.6	1.6	1.6	1.6	11.1	85.7
Gaseous	Carbon disulfide	53	-99.0	0.0	0.0	0.0	0.0	100.0
Gaseous	Acrylonitrile	49	-97.7	0.0	0.0	0.0	0.0	100.0
Gaseous	Chloroprene	46	-99.7	0.0	0.0	0.0	0.0	100.0
Gaseous	1,2,4-Trichlorobenzene	22	-98.1	0.0	0.0	0.0	0.0	100.0
Gaseous	Hexachlorobutadiene	21	-99.7	0.0	0.0	0.0	0.0	100.0
Gaseous	Vinyl Acetate	20	-99.5	0.0	0.0	0.0	0.0	100.0
Gaseous	Ethyl chloride	18	-98.7	0.0	0.0	0.0	0.0	100.0
Gaseous	Acetonitrile	17	-100.0	0.0	0.0	0.0	0.0	100.0
Gaseous	Ethylene oxide	14	-98.8	0.0	0.0	0.0	0.0	100.0
Gaseous	Naphthalene	14	17.3	0.0	0.0	7.1	28.6	85.7
Gaseous	POM (Group 2)	14	-95.5	0.0	0.0	0.0	0.0	100.0
Gaseous	Benzyl chloride	8	-100.0	0.0	0.0	0.0	0.0	100.0
Gaseous	POM (Group 7)	7	-67.3	0.0	0.0	0.0	0.0	100.0
Gaseous	POM (Group 6)	7	-54.7	0.0	0.0	0.0	14.3	85.7
Gaseous	Tribromomethane	7	-99.8	0.0	0.0	0.0	0.0	100.0
Gaseous	POM (Group 5)	6	78.5	16.7	33.3	33.3	66.7	33.3
Gaseous	Bis(2-Ethylhexyl)Phthalate	4	-91.6	0.0	0.0	0.0	0.0	100.0
Gaseous	Chlorine	4	-96.4	0.0	0.0	0.0	0.0	100.0
Gaseous	Biphenyl	4	-87.4	0.0	0.0	0.0	0.0	100.0
Gaseous	Dibenzofuran	3	-100.0	0.0	0.0	0.0	0.0	100.0
Gaseous	Phenol	1	-49.3	0.0	0.0	0.0	100.0	100.0
TSP-Metals	Lead (TSP)	123	-76.0	1.6	4.1	6.5	10.6	96.7
TSP-Metals	Chromium VI	18	1148.8	0.0	0.0	0.0	0.0	0.0

Table 3-2. 2005 Model-to-Monitor Analysis Statistics (Continued)

Type	Pollutant	# Monitors	Average % Difference	%Monitors Within 10%	%Monitors Within 20%	%Monitors Within 30%	%Monitors Within Factor of 2	%Monitors Under-estimated
PM_{10}-Metals	Manganese (PM_{10})	38	-59.9	0.0	0.0	5.3	10.5	94.7
PM_{10}-Metals	Nickel (PM_{10})	37	-50.4	10.8	10.8	16.2	37.8	86.5
PM_{10}-Metals	Lead (PM_{10})	37	-64.4	2.7	8.1	8.1	18.9	97.3
PM_{10}-Metals	Arsenic (PM_{10})	37	-43.7	2.7	16.2	24.3	59.5	94.6
PM_{10}-Metals	Chromium (PM_{10})	36	-27.9	2.8	5.6	8.3	25.0	80.6
PM_{10}-Metals	Cadmium (PM_{10})	32	-32.9	12.5	21.9	28.1	62.5	75.0
PM_{10}-Metals	Beryllium (PM_{10})	26	1430.5	0.0	0.0	0.0	0.0	7.7
PM_{10}-Metals	Selenium (PM_{10})	26	-74.1	3.8	7.7	7.7	7.7	92.3
PM_{10}-Metals	Cobalt (PM_{10})	25	-44.2	4.0	12.0	16.0	36.0	84.0
PM_{10}-Metals	Antimony (PM_{10})	17	-88.0	0.0	0.0	0.0	5.9	100.0
PM_{10}-Metals	Mercury (PM_{10})	2	-74.1	0.0	0.0	0.0	0.0	100.0

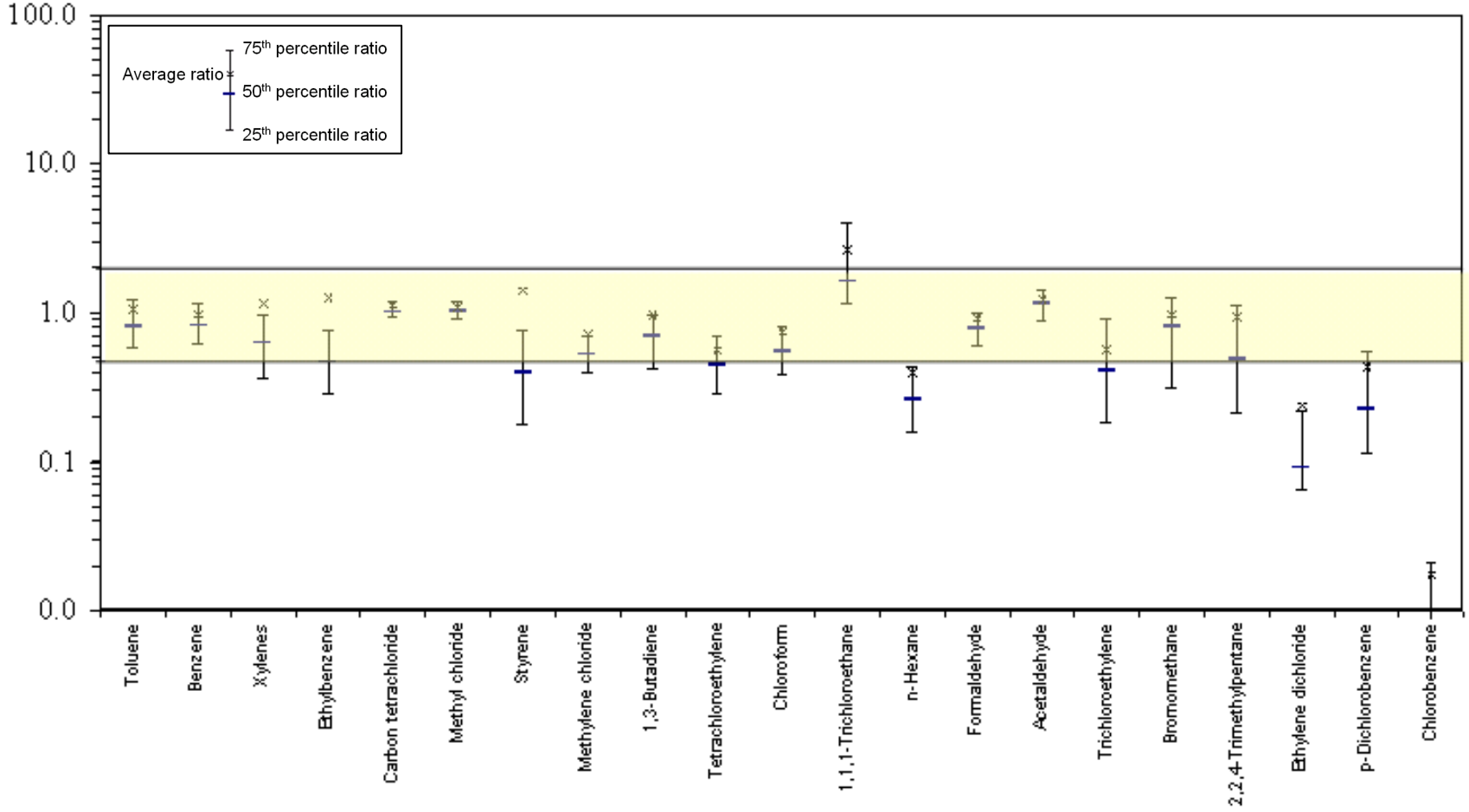

Figure 3-1. Model-to-Monitor Comparisons of Gaseous HAPs (>100 Monitors)

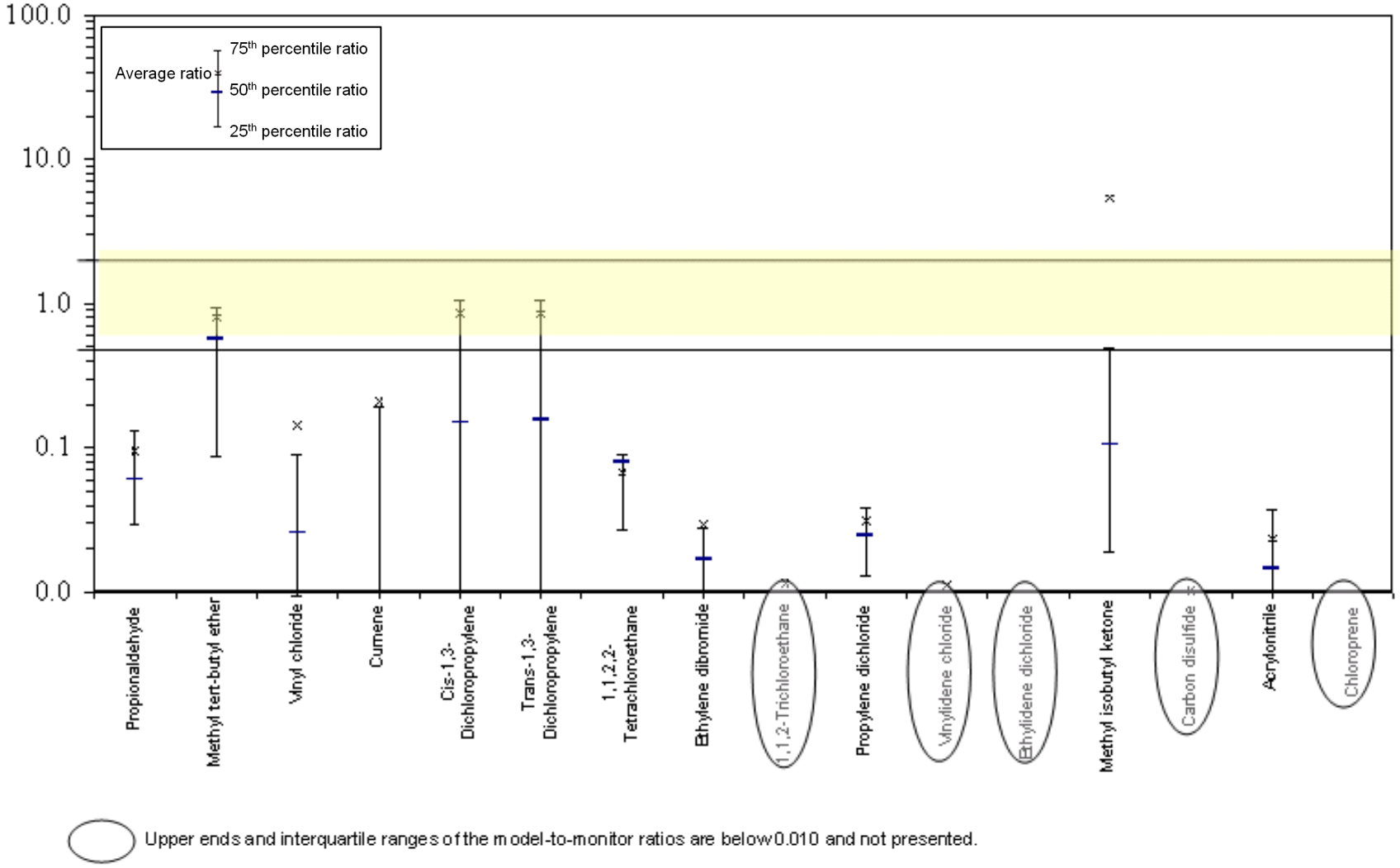

Figure 3-2. Model-to-Monitor Comparisons of Gaseous HAPs (25-100 Monitors)

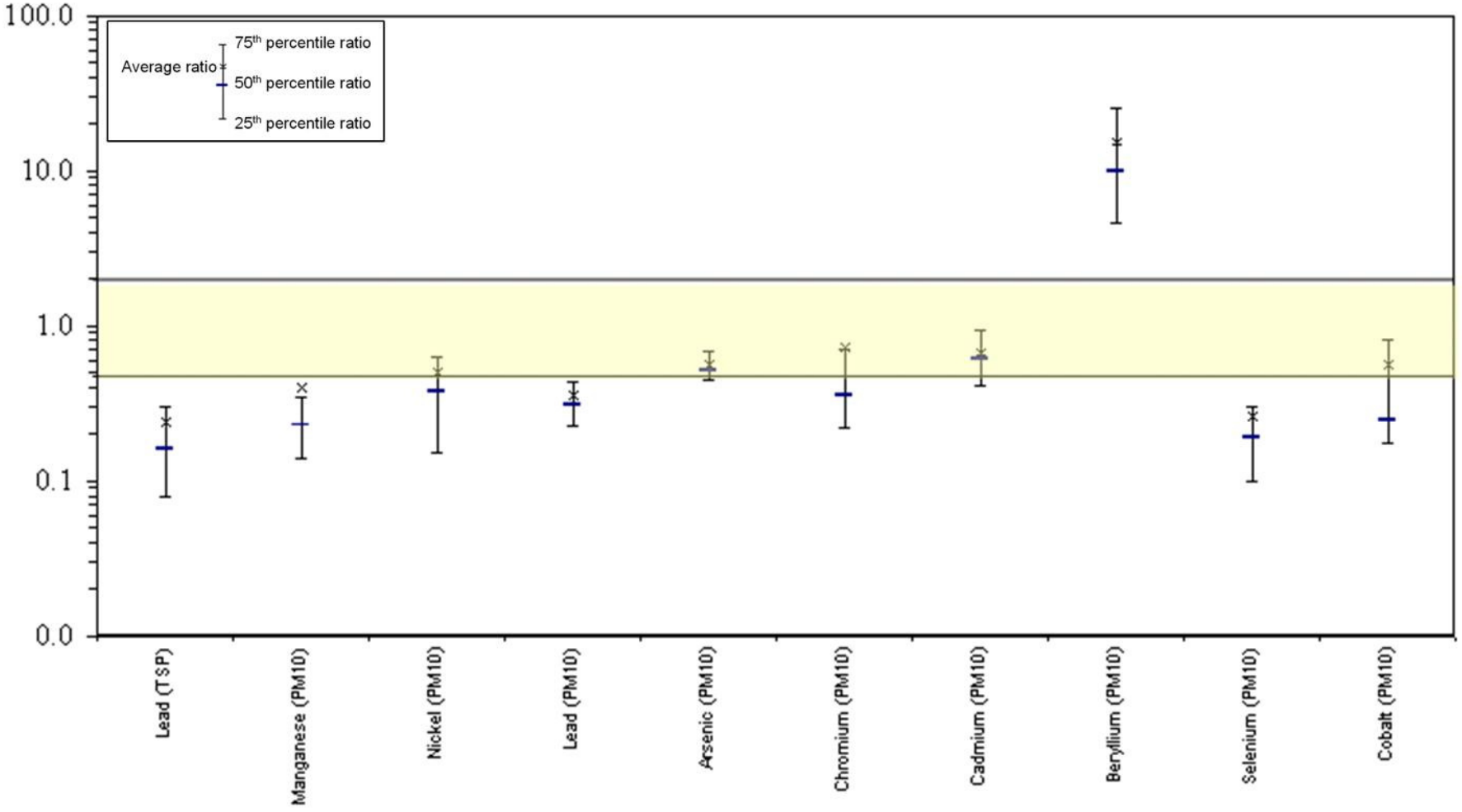

Figure 3-3. Model-to-Monitor Comparisons of Metal HAPs

the box plots do not show extreme percentiles (e.g., 10^{th} and 90^{th}) of the ratios because the extreme percentiles were far from the center of the distribution.

These results show that the interquartile range of model-to-monitor comparisons are within a factor of two for acetaldehyde, arsenic (PM_{10}), benzene, carbon tetrachloride, formaldehyde, methyl chloride, and toluene. The remaining pollutants show various degrees of agreement. Results for the 2005 NATA model-to-monitor comparison are similar to those found in the 2002 national-scale assessment comparisons. The 2005 NATA model still underestimates several pollutants (i.e., 75^{th} percentile ratio is below 0.5), including: *n*-hexane, ethylene dichloride, and chlorobenzene (Figure 3-1); propionaldehyde, vinyl chloride, cumene, 1,1,2,2-tetrachloroethane, ethylene dibromide, 1,1,2-trichloroethane, propylene dichloride, vinylidene chloride, ethylidene dichloride, methyl isobutyl ketone, carbon disulfide, acrylonitrile, and chloroprene (Figure 3-2); and selenium (PM_{10}), manganese (PM_{10}), and lead (PM_{10} and TSP) (Figure 3-3).

The PM_{10} metals appear to have somewhat good agreement with the NATA model, with the exception of beryllium (PM_{10}). Beryllium (PM_{10}) was the only HAP to have its 25^{th} percentile ratio above the factor of 2.

Figures 3-4 through 3-10 present geographic representations of model-to-monitor ratios for seven HAPs: benzene, formaldehyde, carbon tetrachloride, methyl chloride, manganese (PM_{10}), chromium (PM_{10}), and lead (TSP). These types of graphics may be useful in identifying the representativeness of an emission inventory by geographic location. For example, clustering of benzene monitor-to-model results within 10% might suggest that the benzene emission inventory data used in the NATA 2005 for this area may be well-represented. Conversely, clustering of benzene model-to-monitor ratios in a geographic region that were not within a factor of two may indicate that the benzene emission inventory data used in the NATA 2005 may not be well-represented for that area.

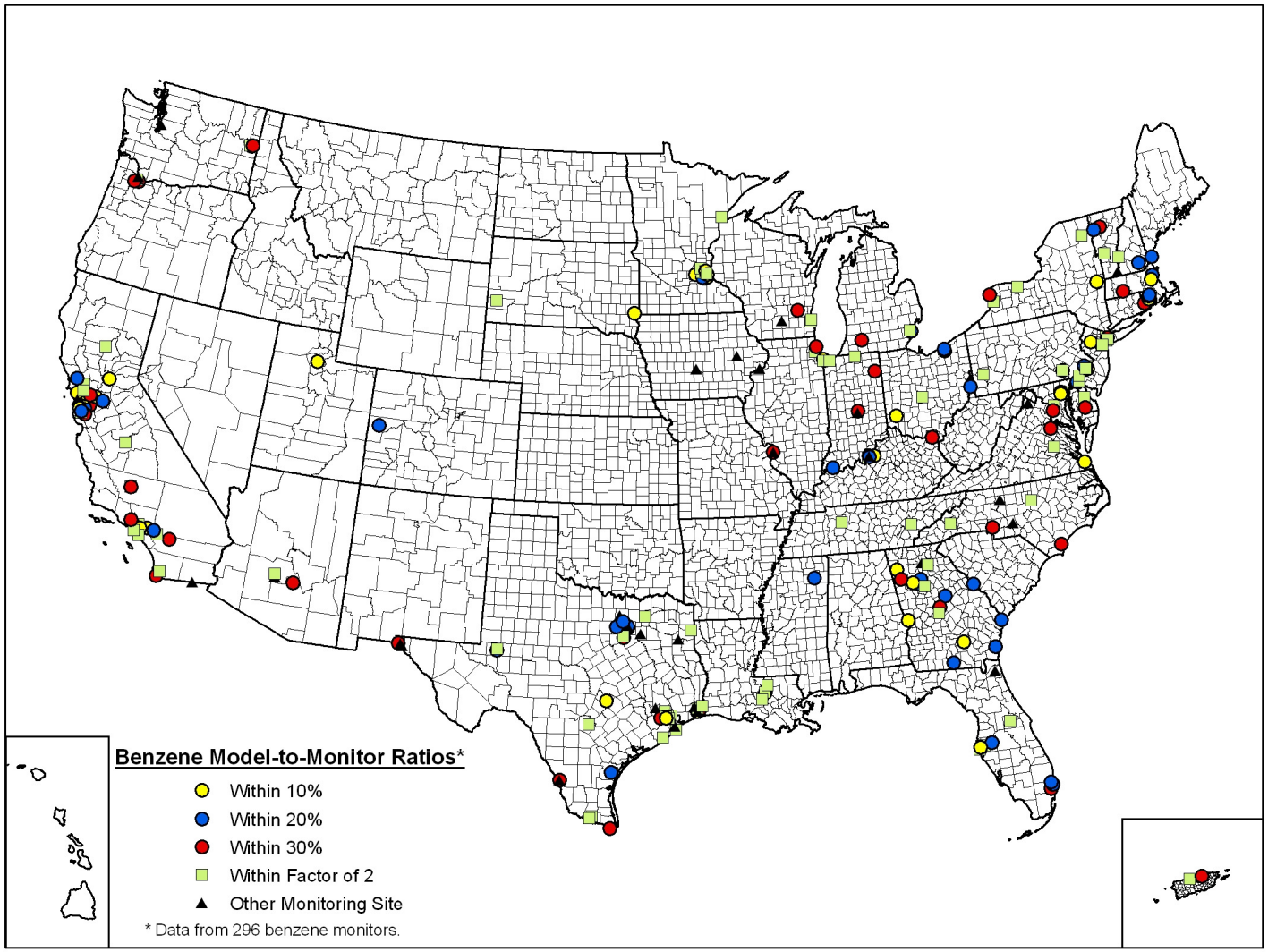

Figure 3-4. Geographic Dispersion of Benzene 2005 Model-to-Monitor Ratios

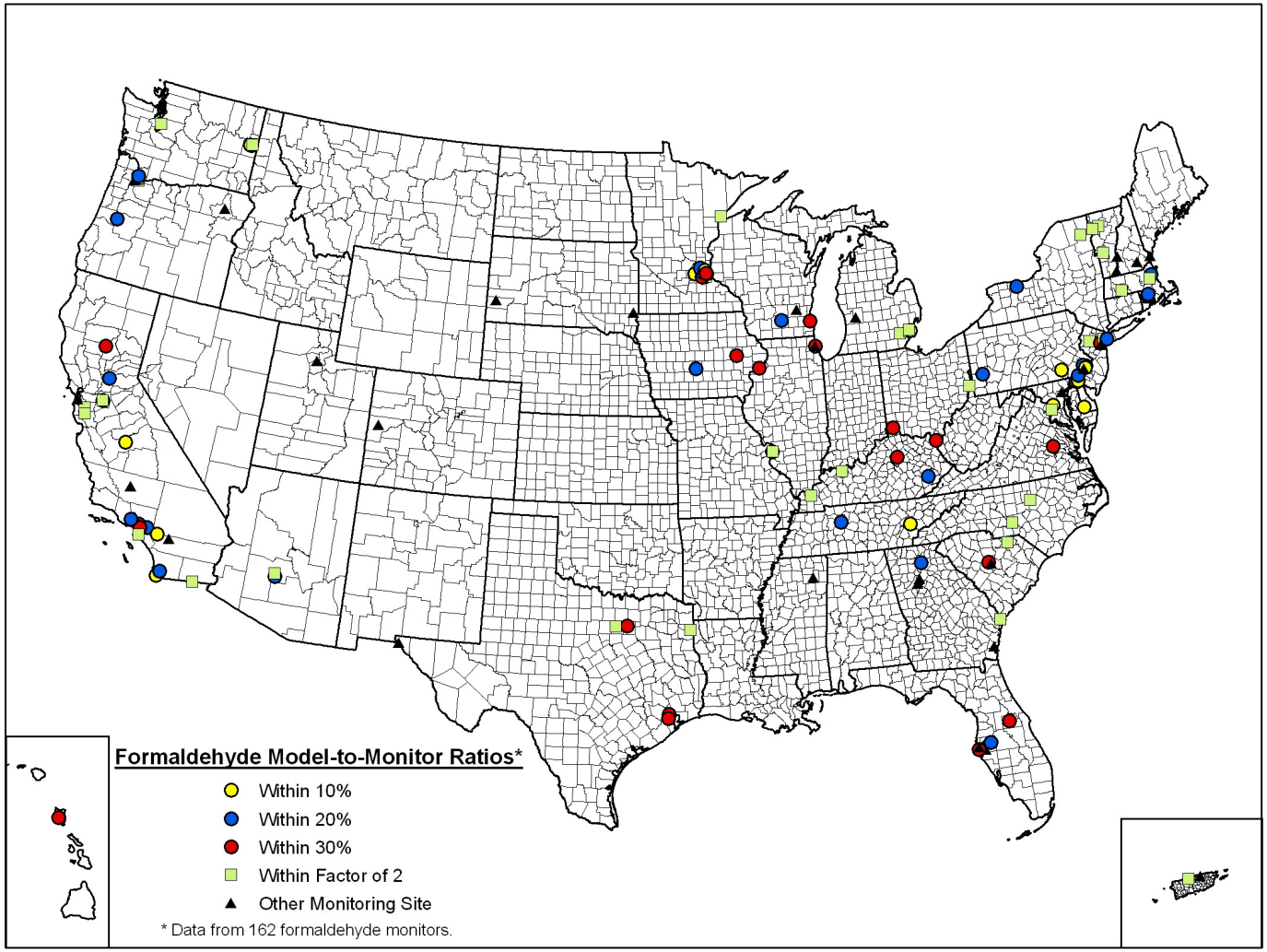

Figure 3-5. Geographic Dispersion of Formaldehyde 2005 Model-to-Monitor Ratios

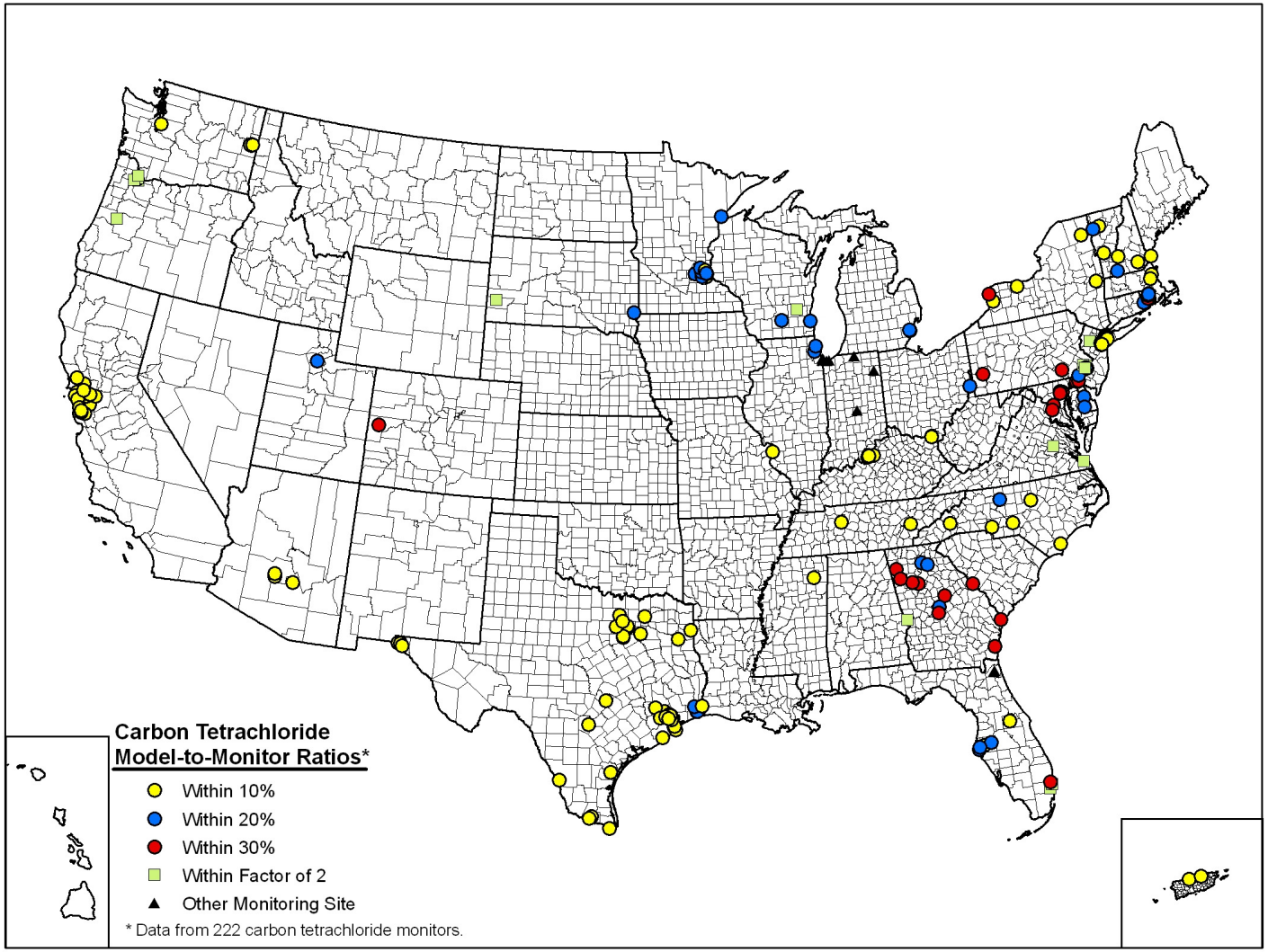

Figure 3-6. Geographic Dispersion of Carbon Tetrachloride 2005 Model-to-Monitor Ratios

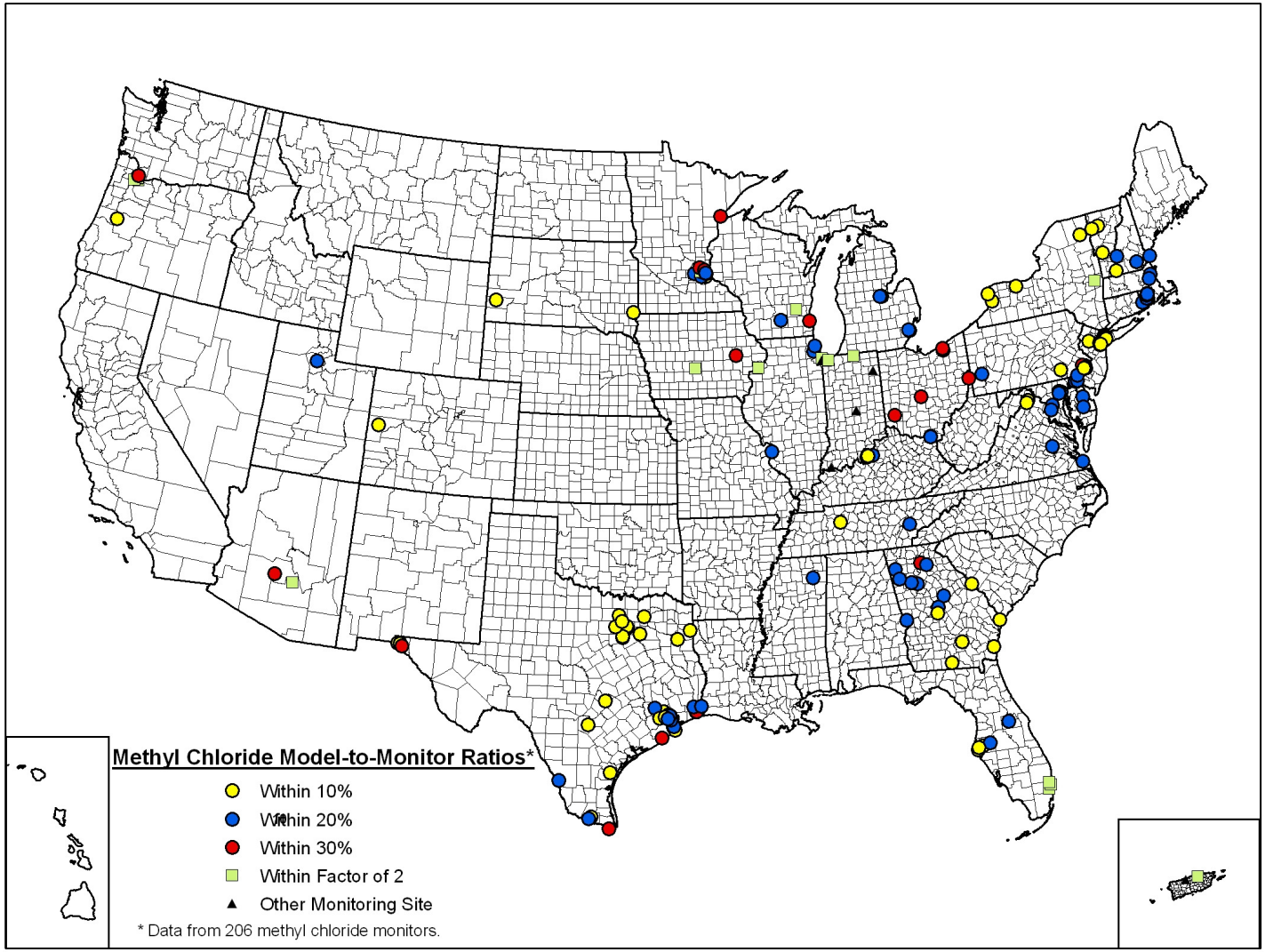

Figure 3-7. Geographic Dispersion of Methyl Chloride 2005 Model-to-Monitor Ratios

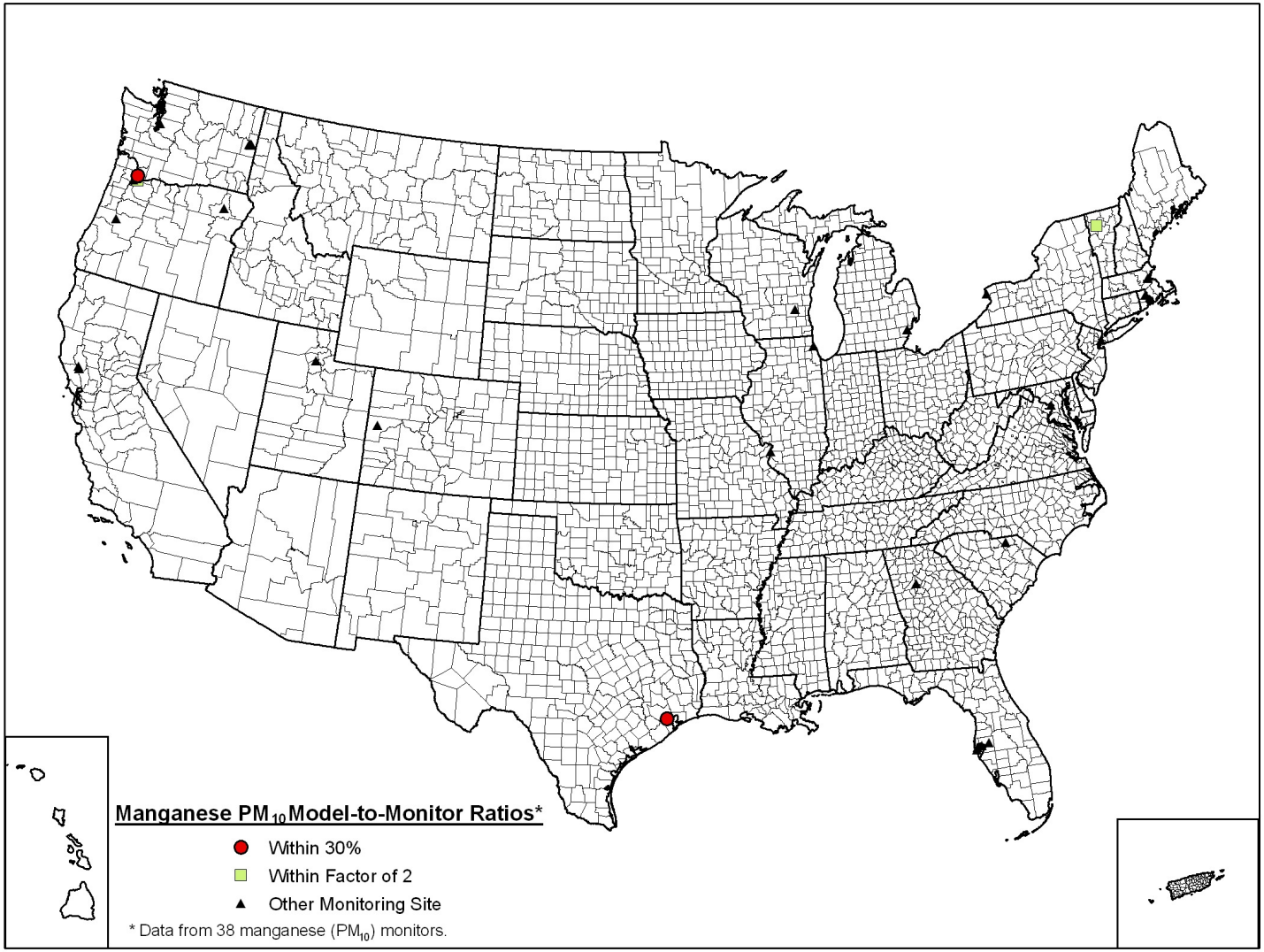

Figure 3-8. Geographic Dispersion of Manganese (PM_{10}) 2005 Model-to-Monitor Ratios

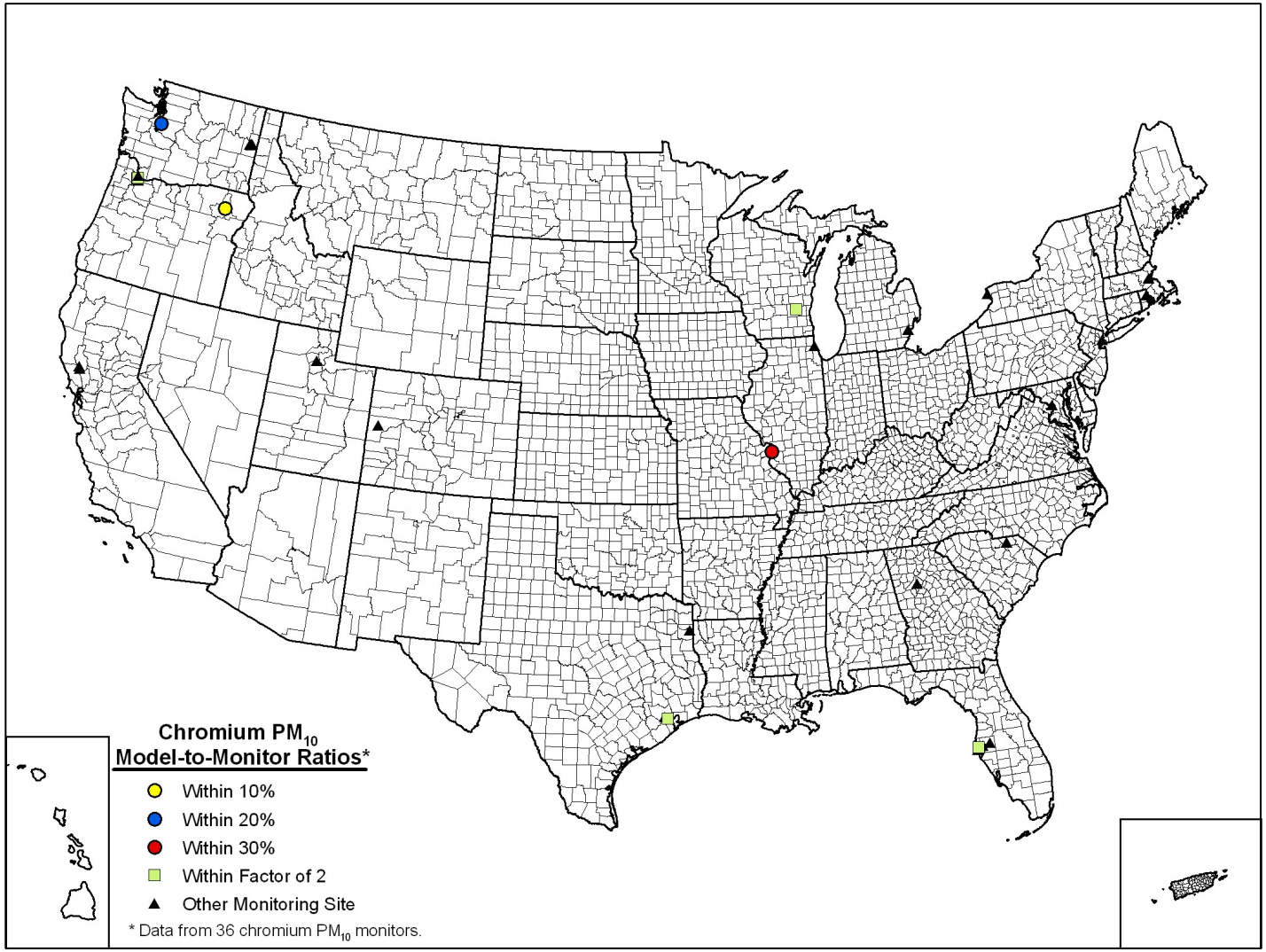

Figure 3-9. Geographic Dispersion of Chromium (PM_{10}) 2005 Model-to-Monitor Ratios

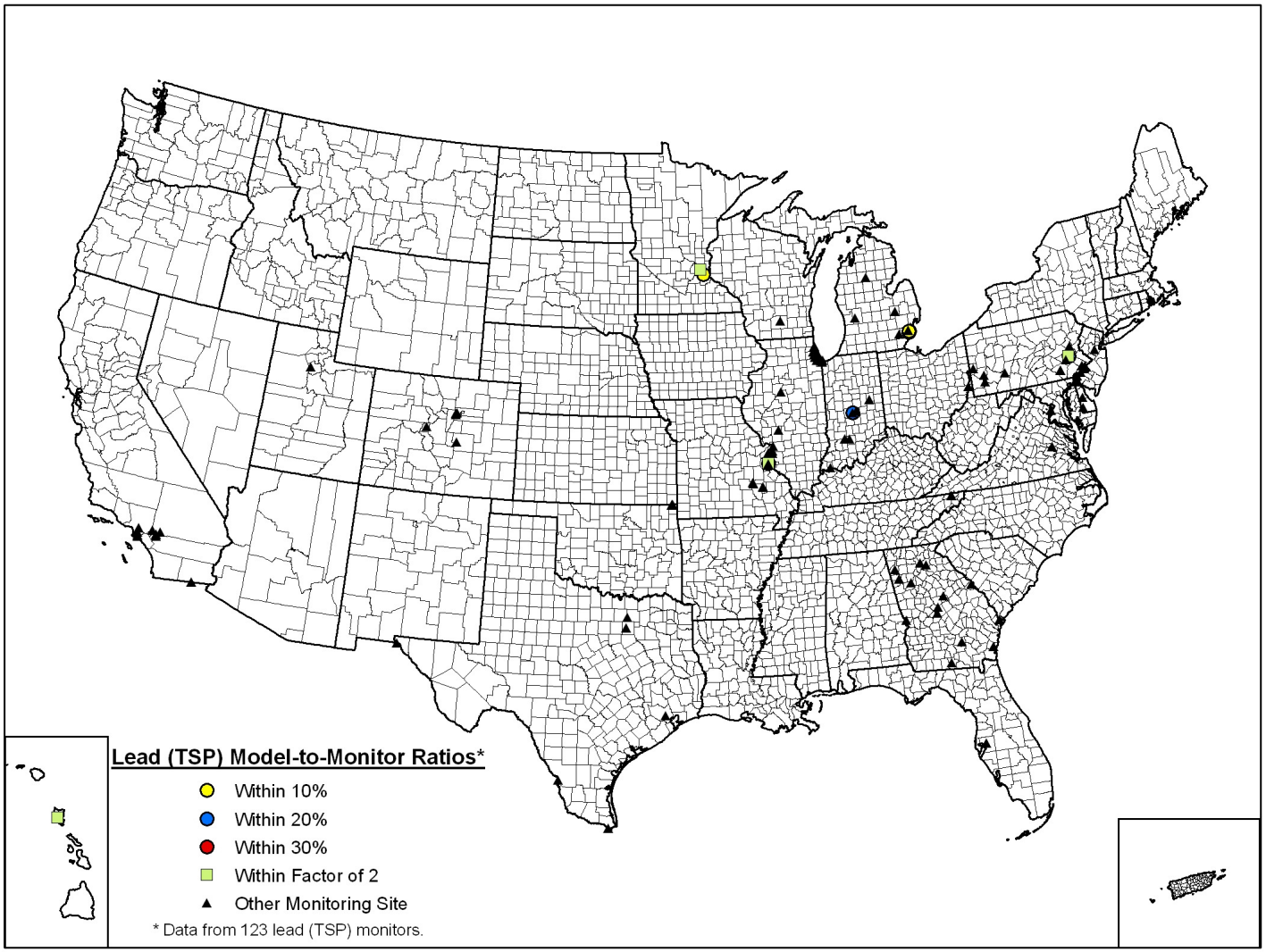

Figure 3-10. Geographic Dispersion of Lead (TSP) 2005 Model-to-Monitor Ratios

Data Considerations - Uncertainties

Earlier in this analysis, we identified several data and model improvements for the 2005 NATA. As a result of these improvements, more pollutants have a median model-to-monitor ratio closer to 1. However, there are still areas in which the model performance could be improved and can be attributed to the following five uncertainties (also identified in the 1996, 1999, and 2002 model-to-monitor comparison results):

1. Emission characterization uncertainties (e.g., specification of source location, emission rates, and release characterization);
2. Meteorological characterization uncertainties (e.g., representativeness);
3. Model formulation and methodology uncertainties (e.g., characterization of dispersion, plume rise, deposition);
4. Monitoring uncertainties; and
5. Uncertainties in background concentrations.

Data Considerations – Under-estimation

Only 10% of all model-to-monitor ratios were between 0.9 and 1.1. While a number of pollutants (32) showed an increasing trend towards a median model-to-monitor ratio of 1, there were several pollutants (17) identified whose 75^{th} percentile values were below a model-to-monitor ratio of 0.5 (i.e., factor of 2), and may be considered as being under-estimated. Reasons for pollutants to be under-estimated in the 2005 model-to-monitor assessment are consistent with previous versions of NATA:

1. The NEI may be missing specific emissions sources (emissions parameters are missing for many of the sources in the NEI);
2. The emission rates may be underestimated. EPA believes the model itself contributed only in a minor way to the underestimation. In many tests evaluating the model performance, the modeled results compared favorably to monitoring data in cases where the emissions and meteorology were accurately characterized and the monitors made more frequent readings;
3. There is uncertainty in the accuracy of the monitor averages, which, in turn, have their own sources of uncertainty. Sampling and analytical uncertainty, measurement bias, and temporal variation can all cause the ambient concentrations to be inaccurate or imprecise representations of the true atmospheric averages; and
4. Background concentrations (pollutants transported large distances and/or formed by photochemical processes in the atmosphere) are poorly characterized. Most of the pollutants for which the model underestimated ambient concentrations were those for which background concentrations were not estimated. If background concentrations are a large fraction of ambient concentrations, the result would be large underestimations in model predictions.

4.0 CONCLUSIONS

This report characterizes the 2005 NATA model-to-monitor comparison. EPA intends to use these data to evaluate strengths and limitations in this and future air toxics modeling assessments. EPA recently completed its fourth national-scale assessment for air toxics across the United States. In this report, the model performance was evaluated for several pollutants by comparing modeled concentrations to monitored concentrations. Over 5,400 model-to-monitor ratios were calculated for 69 HAPs. Less than one-tenth of all model-to-monitor ratios were within 10% (i.e., ratios between 0.9 and 1.1), less than one-fifth of all ratios were within 20% (ratios between 0.8 and 1.2), and approximately one-fourth of all ratios were within 30% (ratios between 0.7 and 1.3).

The following three questions were used to guide the study:

- ***Which pollutants are in good agreement between the ambient concentrations and the NATA 2005 model?*** Good agreement (i.e., interquartile values within a factor of two) were seen for the following pollutants: acetaldehyde, arsenic (PM_{10}), benzene, carbon tetrachloride, formaldehyde, methyl chloride, and toluene.

- ***Which pollutants are under-predicted between the ambient concentrations and the NATA 2005 model?*** Under-prediction (upper bound of the interquartile range less than a factor of two) was seen for the following pollutants: acrylonitrile, carbon disulfide, chlorobenzene, chloroprene, cumene, ethylene dibromide, ethylene dichloride, ethylidene dichloride, *n*-hexane, methyl isobutyl ketone, propionaldehyde, propylene dichloride, selenium (PM_{10}), 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, vinyl chloride, and vinylidene chloride.

- ***Which pollutants are over-predicted between the ambient concentrations and the NATA 2005 model?*** Over-prediction (lower bound of the interquartile greater than a factor of two) was seen for beryllium (PM_{10}).

HAPs in which 80% of their monitored values were within a factor of 2 were benzene (82%), carbon tetrachloride (95%), methyl chloride (98%), and acetaldehyde (87%). "Factor of 2" ratios (ratios between 0.5 and 2.0) accounted for 44% of the model-to-monitor ratios. In general, gaseous HAPs tended to have average and median model-to-monitor ratios closer to 1, while average and median model-to-monitor ratios for metal HAPs were often under-estimated.

Appendix A. HAPs Not Evaluated in this Assessment

Table A-1. HAPs Not Evaluated in this Assessment Due To Limited or No Ambient Measurements Data

1,1-Dimethyl hydrazine	Acrylamide	Dimethyl carbamoyl chloride	Methyl methacrylate
1,2-Dibromo-3-chloropropane	Acrylic acid	Dimethyl formamide	Methylene diphenyl diisocyanate (MDI)
1,2-Diphenylhydrazine	Allyl chloride	Dimethyl phthalate	*N,N*-Diethyl aniline (*N,N*-Dimethylaniline)
1,2-Epoxybutane	Aniline	Dimethyl sulfate	Nitrobenzene
1,2-Propylenimine (2-Methyl aziridine)	Asbestos	Epichlorohydrin (l-Chloro-2,3-epoxypropane)	*N*-Nitrosodimethylamine
1,3-Propane sultone	Benzidine	Ethyl acrylate	*N*-Nitrosomorpholine
1,4-Dioxane (1,4-Diethyleneoxide)	Benzotrichloride	Ethyl carbamate (Urethane)	*N*-Nitroso-*N*-methylurea
2,3,7,8-Tetrachlorodibenzo-*p*-dioxin	*beta*-Propiolactone	Ethylene glycol	*o*-Anisidine
2,4,5-Trichlorophenol	Bis(chloromethyl)ether	Ethylene imine (Aziridine)	*o*-Toluidine
2,4,6-Trichlorophenol	Calcium cyanamide	Ethylene thiourea	Parathion
2,4-D, salts and esters	Captan	Fine mineral fibers	Pentachloronitrobenzene (Quintobenzene)
2,4-Dinitrophenol	Carbaryl	Glycol ethers	Pentachlorophenol
2,4-Dinitrotoluene	Carbonyl sulfide	Heptachlor	Phosgene
2,4-Toluene diamine	Catechol	Hexachlorobenzene	Phosphine
2,4-Toluene diisocyanate	Chloramben	Hexachlorocyclopentadiene	Phosphorus
2-Acetylaminofluorene	Chlordane	Hexachloroethane	Phthalic anhydride
2-Chloroacetophenone	Chloroacetic acid	Hexamethylene-1,6-diisocyanate	Polychlorinated biphenyls (Aroclors)
2-Nitropropane	Chlorobenzilate	Hexamethylphosphoramide	*p*-Phenylenediamine
3,3-Dichlorobenzidene	Chloromethyl methyl ether	Hydrazine	Propoxur (Baygon)
3,3-Dimethoxybenzidine	Coke Oven Emissions	Hydrochloric acid	Propylene oxide
3,3'-Dimethyl benzidine	Cresols/Cresylic acid (isomers and mixture)	Hydrogen fluoride (Hydrofluoric acid)	Quinoline
4,4'¬-Methylenedianiline	Cyanide Compounds	Hydroquinone	Quinone
4,4-Methylene bis(2-chloroaniline)	DDE	Isophorone	Radionuclides (including radon)
4,6-Dinitro-o-cresol, and salts	Diazomethane	Lindane (all isomers)	Styrene oxide
4-Aminobiphenyl	Dibutylphthalate	Maleic anhydride	Titanium tetrachloride
4-Nitrobiphenyl	Dichloroethyl ether (Bis(2-chloroethyl)ether)	Methanol	Toxaphene (chlorinated camphene)
4-Nitrophenol	Dichlorvos	Methoxychlor	Triethylamine
Acetamide	Diethanolamine	Methyl hydrazine	Vinyl acetate
Acetophenone	Diethyl sulfate	Methyl iodide (Iodomethane)	Vinyl bromide
Acrolein	Dimethyl aminoazobenzene	Methyl isocyanate	